

RESEARCH MEMORANDUM

VARIATION IN SMOKING TENDENCY AMONG LOW MOLECULAR
WEIGHT HYDROCARBONS

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SUMMARY

An investigation was made of the variations in smoking tendency among 38 gaseous and liquid pure hydrocarbon compounds when burned as diffusion flames in still air. The maximum rates at which the fuels could be burned smoke-free varied as follows: n-paraffins > iso-paraffins > monoolefins > alkynes > aromatics. Cyclic paraffins and olefins as well as diolefins were also studied. Their position overlapped the trends of several of the series presented.

Variations in smoking tendencies within the given homologous series were rather complex, but a tentative explanation is that the greater the strength of the carbon bonds or skeleton of the hydrocarbon molecule, the greater will be its tendency to form smoke during combustion. From this suggested explanation a possible mechanism based on dehydrogenation and subsequent polymerization of the carbon nuclei was proposed as the initial step involved in the formation of smoke.

INTRODUCTION

In recent years considerable effort has been made to determine the factors and mechanisms which govern the formation of smoke during the burning of fuels, so that, eventually, methods of controlling smoke formation can be devised (references 1 to 3). Particular emphasis has been placed on the problem of preventing smoke formation during the burning of fuels in combustion chambers. Since the type of hydrocarbon present in a fuel is known to affect smoke formation (references 4 and 5), an investigation was conducted as part of the fundamental combustion program at the NACA Lewis laboratory to determine the maximum rate at which various pure hydrocarbons could be burned without producing smoke. From this investigation, it was hoped that the effects on smoking of such variables as chain length, chain branching, degree of unsaturation, position of unsaturation, and ring size could be evaluated and an explanation found to account for the variations.

Previous investigators have determined smoking tendencies by measuring the maximum height to which a flame would burn without smoking (references 4 and 5). In the present work pure hydrocarbons were burned in still air as diffusion flames from wicks and burner tubes, and the maximum quantity of hydrocarbon which could be burned smoke-free in a given time was used as the criterion of smoking tendency. In addition to this modification in measuring smoking tendencies, the types of hydrocarbon studied have been extended beyond those previously investigated.

An interpretation of the data obtained in the present work has led to a proposal that differences in the smoking tendencies of hydrocarbons can be related to the relative strengths of their carbon-carbon and carbon-hydrogen bonds.

APPARATUS AND PROCEDURE

The determination of the relative rates at which gaseous hydrocarbons could be burned smoke-free was made by passing the gaseous fuels through a flowmeter, calibrated for each hydrocarbon, and then burning them as diffusion flames from a burner tube of 9 millimeter diameter (fig. 1(a)). The maximum fuel flow before the flame began to smoke was determined. A visual observation was used for detecting the smoking point.

The liquid hydrocarbons were placed in a wick lamp and weighed. The wick lamp was adjusted to the smoking point by raising or lowering the height of the wick tip through a small condenser (fig. 1(b)). The vapor pressure and, consequently, the amount of fuel supplied to the flame could be slightly increased or decreased by varying the temperature of the water flowing through the condenser. After the sample had burned for a given interval of time at its incipient smoking point, it was reweighed and the amount of fuel burned per unit time was calculated.

It was not known whether the results obtained by burning gaseous fuels from a tube and liquid fuels from a wick could be placed on the same relative scale. Consequently, a bomb was used to hold several of the vaporized liquid fuels which were then burned in the gaseous phase from the same size tube as had been used for the gaseous hydrocarbons (fig. 1(c)). Within the experimental limit of about ± 2 percent, it was found that the same results were obtained when the liquids were either vaporized and burned from the tube or burned from the wick lamp.

A chimney of 47 millimeter diameter and 300 millimeter height was placed level with the burner tube port or wick tip in all experiments to keep the flames erect and stable. Since changes in the size and position of this chimney or other variation in the geometry of the apparatus would change the smoking characteristics of the flame, the results of this investigation are relative.

RESULTS AND DISCUSSION

The hydrocarbons employed in the present investigation and the maximum fuel flow at which each could be burned without smoking are given in table I. In figure 2 the maximum rate (g/sec) at which the sample could be burned smoke-free is plotted against the number of carbon atoms in the compound for a ready comparison of the data.

As a class, the *n*-paraffins showed the largest rate of fuel burned smoke-free; however, this rate decreased with increasing chain length. If the paraffin chain was branched, the rate at which fuel could be burned smoke-free was markedly reduced. For the cycloparaffins the rate of fuel burned smoke-free increased with increasing ring size; however, this rate was less than that of the *n*-paraffins or the 2-methyl paraffins. In the one case investigated, adding a side chain to the ring decreased the rate of fuel burned smoke-free.

The straight-chain monoolefins did not show the same trend as the *n*-paraffins. As shown in figure 2, the rate at which the olefins could be burned smoke-free decreased from ethene to butene and then increased to decene-1. Within the limits of experimental error, butene-1 and butene-2 showed the same rate of fuel burned smoke-free. This similarity probably results from the fact that in a diffusion flame the fuel is subjected to temperatures of the order of 800° C before reaching a region of oxygen (reference 1). Temperatures of such magnitude are capable of isomerizing butene-1 to butene-2 (reference 6). Consequently, butene-2 is probably the only compound being burned, and the observed smoking tendencies would be the same for both fuels. The rate at which cyclic olefins could be burned smoke-free increased with increasing ring size, but was less than the corresponding straight-chain monoolefin. The diolefins also showed a greater tendency to smoke than the monoolefins.

The straight-chain monoalkynes showed a very slight increase in the rate of fuel burned smoke-free from acetylene to hexyne-1.

Several aromatic hydrocarbons were also studied. As can be seen in figure 2, the aromatics showed the greatest tendency to smoke. The rate at which the sample could be burned smoke-free decreased with increasing length of the side chain.

It was observed that a plot of the reciprocal fuel flow in milliliters of gas per second produced a series of straight lines as shown in figure 3. If it is permissible to extrapolate these lines, the amount of higher molecular weight compounds which could be burned smoke-free might be calculated.

In table II a relative comparison of smoking properties is made among those compounds reported by Clarke, Hunter, and Garner (reference 4) which were also studied in this investigation. Although the

values reported in reference 4 are the maximum smoke-free flame height and the values from the present study are the maximum smoke-free fuel flow, comparison showed the two values to be approximately proportional. Dividing the data of reference 4 by two, which was determined mathematically as the factor which would put the values on the same numerical scale, gave relative values which compared quite closely with those from the present work.

Minchin (reference 5) also reports the smoking tendencies of numerous hydrocarbons. Some of the values obtained by reference 5 are compared with the values from the present investigation in table II. While the relative trends within a given homologous series are in fair agreement, the relative variation from one series to another is not. For example, from reference 4 and the data reported herein there is approximately a threefold variation between hexane and hexene. The variation in Minchin's values is about eightfold. Between hexane and benzene, the results of reference 4 and the present report both show a factor of about 20; Minchin's results show a factor of about 37. A further comparison of Minchin's data was not made because the specific compounds which he studied are not tabulated. His data were presented in graph form with only the homologous series name given. An attempt to select specific compounds from such a plot may have already led to certain errors because isomeric compounds cannot be distinguished. Some error may also have been made in reading the numerical values from the graph. It would seem, however, that this error would not be great enough to account for some of the variations.

Few theories have been presented to account for the variation in smoking tendencies among different fuel types. In reference 4, the relation between tendency to smoke and the carbon-hydrogen ratio of hydrocarbons is discussed. It is concluded, however, that other factors must also have an important bearing on the smoking tendency. An equation based on the oxygen requirements of a flame was proposed by Minchin to predict the maximum smoke-free flame height. A comparison of the values predicted by this equation with the values obtained in the present investigation are shown in table III. As can be seen from the table, the equation does not give very satisfactory agreement in predicting the relative trends within an homologous series or in the trends among hydrocarbon types. The basis on which the equation is founded would seem to have considerable merit, but in its present form it does not appear to predict the differences in smoking tendency which were observed in this research.

The following proposal, which attempts to relate smoking tendency to increasing stability of the carbon chain or skeleton, is tentatively suggested as a possible explanation for the trends in the data reported in this study. This proposal is, of course, speculative because of the complexity of the variation in smoking tendency with fuel type.

If a comparison is made among compounds of the same number of carbon atoms, the most unsaturated compounds show the smallest rate of fuel being burned smoke-free. In compounds of two carbon atoms, for example, the rate of fuel burned smoke-free decreased from ethane to ethene to acetylene. These three compounds represent a change in structure from single- to double- to triple-bonded carbon atoms. This change in bond structure is accompanied by an increase in the amount of energy holding the carbon atoms together since the bond strengths of single, double, and triple carbon-carbon bonds are approximately 80, 150, and 200 kilocalories per mole, respectively (reference 7). In figure 4 are shown the maximum smoke-free fuel flows in grams per second against the total carbon-carbon bond strengths for compounds of 2, 3, and 4 carbon atoms. It would seem that the most thermally stable molecules show the greatest tendency to smoke.

While there is little question that the unsaturated compounds possess increasing bond strengths, the variation in bond strengths among the isomeric paraffins is less definite. However, from values of the carbon-carbon bond strength for isomeric paraffins as reported by Burawoy (reference 8), isoparaffins possess about 5 kilocalories per mole more total carbon-carbon bond strength than *n*-paraffins. Data on heat of formation also indicate that isoparaffins are more stable than the *n*-paraffins (reference 9).

A comparison of the stability of the carbon chain was not made among compounds of different numbers of carbon atoms. Such a comparison is meaningless since any variation in ease of breaking the carbon-carbon bonds is overshadowed by the additional increase in the amount of carbon existing in the compound. In the paraffin series, for example, the carbon-carbon bonds in *n*-octane may be weaker than in ethane, but there would be four times as many carbon atoms present in *n*-octane. However, in addition to plotting the total carbon-carbon bond strength for compounds of a given number of carbon atoms, the total carbon-carbon bond strength divided by the number of carbon atoms in the compound was plotted against maximum smoke-free fuel flow (g/sec) for all compounds studied (fig. 5). The qualitative relation observed in figure 4 seems to be present in figure 5, but the relation does not appear to be quantitative. There are undoubtedly other factors adding to the stability of the carbon chain or skeleton in a flame which must be taken into consideration.

One of those factors is hyperconjugation. Wheland (reference 10) reports that such compounds as propene and butene are stabilized as a result of hyperconjugation, and that hyperconjugation in propene produces a resonance energy of about the same order of magnitude as does the conjugation between two double bonds, as in butadiene. In addition to the effect this factor would have on the data in figure 5, it is possible that the apparent minimum in the olefin curve around propene

and butene (fig. 2) results from the increased stability of these two compounds. The effect is probably carried over to a lesser extent in some of the higher molecular weight olefins.

Some additional explanation is also necessary to account for the trends of the cycloparaffins. The stability of the ring increases from cyclopropane to cyclohexane and yet the rate of fuel burned smoke-free also increases. The low rate for cyclopropane may be explained on the basis that cyclopropane readily isomerizes to propene (reference 11) at those temperatures encountered when entering the flame. Consequently, the fuel-flow rate of cyclopropane should be close to that of propene. This agreement is shown experimentally in figure 2. The thermal decomposition of cyclopentane and cyclohexane probably leads to compounds which are more readily burned than propene.

In the preceding discussion an attempt has been made to relate smoking tendencies to increasing stability of the carbon chain or skeleton. While the relation is not strictly quantitative and seems weak at certain points, no other variable seemed to explain the trends as adequately. If it is permissible to conclude that increases in the stability of the molecule accompany increases in smoking tendencies, a possible mechanism for the formation of smoke may be deduced.

As previously stated the bond strengths of single, double, and triple carbon-carbon bonds are about 80, 150, and 200 kilocalories per mole, respectively. The carbon-hydrogen bond strength is approximately 100 kilocalories per mole (reference 7). These numbers would indicate that in the saturated compounds the carbon-carbon bonds would be broken more readily than the carbon-hydrogen bonds. As the carbon-carbon bond strength or stability of the carbon skeleton increases, the carbon-hydrogen bonds would become relatively easier to break. A dehydrogenation process may therefore be taking place as the stability of the carbon skeleton increases. Removal of the hydrogen atoms would probably leave behind either partially or totally dehydrogenated carbon nuclei which might polymerize to form smoke. In a previous investigation by Arthur (reference 2), it was demonstrated that suppression of the formation of hydrogen atoms in a flame accompanied suppression of smoke formation. Thorp, Long, and Garner (reference 12) reported that carbon formation was reduced in a benzene flame when hydrogen was substituted for nitrogen as the carrier gas. It is also concluded in reference 12 that this decrease in carbon resulted from the suppression of dehydrogenation. A relation between ease of removal of hydrogen atoms and smoking therefore appears to be in agreement with reported experimental findings.

SUMMARY OF RESULTS

An investigation of the variations in smoking tendencies among 38 pure hydrocarbon compounds gave the following results:

1. The maximum rates (g/sec) at which the fuels could be burned smoke-free varied as follows: n-paraffins > isoparaffins > monoolefins > alkynes > aromatics.

2. Variations within the homologous series were as follows:

- (a) Paraffins - maximum rate of fuel burned smoke-free decreased with increasing chain length. Rate also decreased with branching.
- (b) Olefins - rate of fuel burned smoke-free decreased from ethene to butene, but then increased to decene.
- (c) Cyclic olefins and paraffins - rate increased with increasing ring size but was less than the rate of the corresponding straight-chain compound.
- (d) Alkynes - rate increased very slightly from acetylene to hexyne-1.
- (e) Aromatics - rate of fuel burned smoke-free decreased from benzene to n-propylbenzene.

3. An explanation relating increased stability of the carbon bonds or skeleton to increasing smoking tendencies is tentatively suggested to explain these variations. A possible mechanism for the formation of smoke based on dehydrogenation and polymerization of carbon nuclei is also proposed.

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TABLE I - RELATIVE MAXIMUM SMOKE-FREE FUEL-FLOW RATES

Compound	Number of carbon atoms	Maximum fuel flow		1 ml/sec	Total carbon-carbon bond strength (kcal/mole)	Total carbon-carbon bond strength per number of carbon atoms
		g/sec	ml/sec			
Ethane	2	16.52 10^{-3}	13.70	0.073	80	40
Propane	3	10.15	5.78	.173	160	53
Butane	4	8.60	3.69	.271	240	60
Pentane	5	8.04 ^a (8.10)	2.78	.360	320	64
Hexane	6	7.59	2.20	.455	400	67
Heptane	7	7.43	1.85	.541	480	69
Octane	8	7.22	1.58	.634	560	70
Nonane	9	7.03	1.37	.732	640	71
Isobutane	4	4.01	1.72	0.581	245	61
Isohexane	6	5.43	1.57	.636	405	67.5
Isononane	9	5.36	1.04	.959	645	72
Neopentane	5	2.49	.86	1.163	329	66
Cyclopropane	3	1.08	0.64	1.562	240	80
Cyclopentane	5	2.64	.94	1.064	400	80
Cyclohexane	6	4.20	1.25	.803	480	80
Methylcyclopentane	6	2.28	.68	1.477	480	80
Ethene	2	5.74	5.10	0.196	150	75
Propene	3	1.54	.91	1.099	230	77
Butene-1	4	1.21	.54	1.852	310	77.5
Butene-2	4	1.28	.57	1.755	310	77.5
Isobutene	4	1.10	.49	2.040	315	79
Pentene-1	5	2.35 ^a (2.43)	.84	1.198	390	78
Hexene-1	6	2.60	.77	1.300	470	78
Heptene-1	7	2.92	.74	1.338	550	79
Heptene-2	7	2.84	.71	1.410	550	79
Decene-1	10	3.87	.69	1.453	790	79
Butadiene-1,3	4	0.15	0.07	14.286	380	95
2,5-Dimethylhexadiene-1,5	8	.49	.11	9.009	710	89
Cyclopentene	5	0.43	0.16	6.396	470	94
Cyclohexene	6	2.07	.63	1.598	550	92
Acetylene	2	0.43	0.41	2.439	200	100
Propyne-1	3	.43	.27	3.704	280	93
Pentyne-1	5	.45	.16	6.098	440	88
Hexyne-1	6	.46	.14	7.241	520	87
Benzene	6	0.34	0.11	9.346	798	133
Toluene	7	.23	.06	16.131	878	125
Ethylbenzene	8	.18	.04	23.81	958	120
n-Propylbenzene	9	.17	.035	28.571	1038	115

^aResults obtained by use of pressure bomb.

TABLE II - COMPARISON OF EXPERIMENTAL RESULTS WITH
VALUES FROM THE LITERATURE

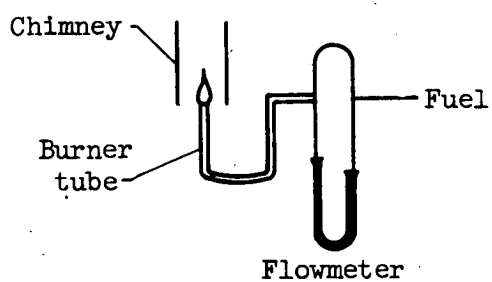


Reference	Compound	Flame height h (cm)	$\frac{h}{2.0}$	$\frac{h}{1.4}$	NACA maximum fuel flow (g/sec)
4	n-Pentane	15.5	7.75		8.04×10^{-3}
	n-Heptane	15.9	7.95		7.43
	Pentene	4.8	2.40		2.35
	Hexene	5.1	2.55		2.60
	Heptene	6.4	3.20		2.85
	Decene	7.0	3.50		3.87
	Cyclopentane	6.2	3.10		2.64
	Cyclohexane	7.7	3.85		4.20
	Cyclohexene	4.3	2.15		2.07
	Benzene	.9	.45		.34
	Toluene	1.0	.50		.23
5	Hexane	16.0		11.2	7.59×10^{-3}
	Nonane	11.1		7.76	5.36
	Hexene	1.94		1.36	2.60
	Decene	2.5		1.75	3.87
	Cyclohexane	1.94		1.36	4.20
	Benzene	.44		.31	.34
	Toluene	.45		.31	.23
	Ethylbenzene	.42		.29	.18

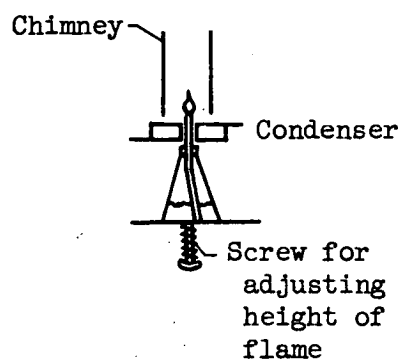
TABLE III - COMPARISON OF VALUES CALCULATED BY
 FORMULA OF MINCHIN WITH THOSE OBTAINED
 IN PRESENT STUDY



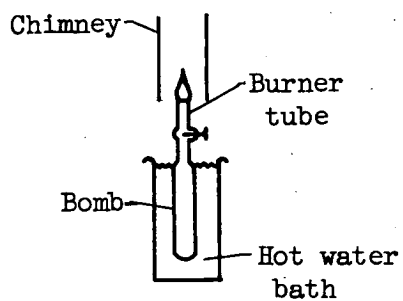
Compound	Minchin's calculated flame height (cm)	NACA maximum fuel flow (g/sec)
Ethane	3.14	16.52
Propane	7.97	10.15
Butane	17.78	8.60
Pentane	27.80	8.04
Hexane	27.23	7.59
Heptane	21.39	7.43
Octane	16.46	7.22
Nonane	13.13	7.03
Ethene	0.79	5.74
Propene	1.15	1.54
Butene	1.47	1.25
Pentene	1.74	2.35
Hexene	1.94	2.60
Heptene	2.09	2.88
Decene	2.35	3.87
Butadiene-1,3	0.72	0.15
2,5-Dimethyl- hexadiene-1,5	.74	.49
Acetylene	0.42	0.43
Propyne	.58	.43
Pentyne	.84	.45
Hexyne	.95	.46
Cyclopropane	1.15	1.08
Cyclopentane	1.74	2.64
Cyclohexane	1.94	4.20
Methylcyclopentane	2.09	2.28
Cyclopentene	0.58	0.43
Cyclohexene	.95	2.07
Benzene	0.43	0.34
Toluene	.49	.23
Ethyl benzene	.54	.18
n-Propylbenzene	.58	.17



(a) Gases.



(b) Liquids.



(c) Liquids.

Figure 1. - Diagram of apparatus.

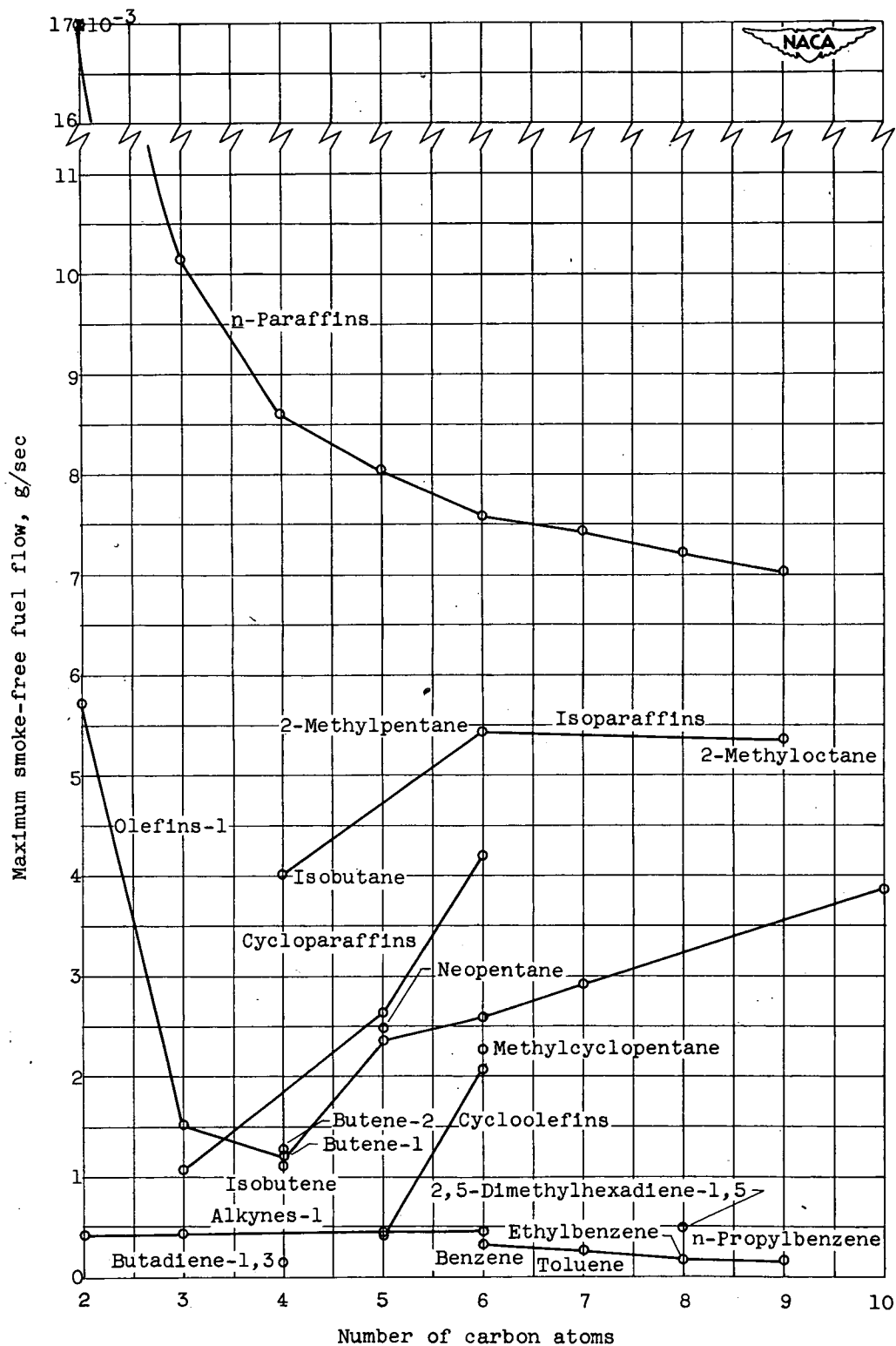


Figure 2. - Variation of maximum smoke-free fuel flow with number of carbon atoms.

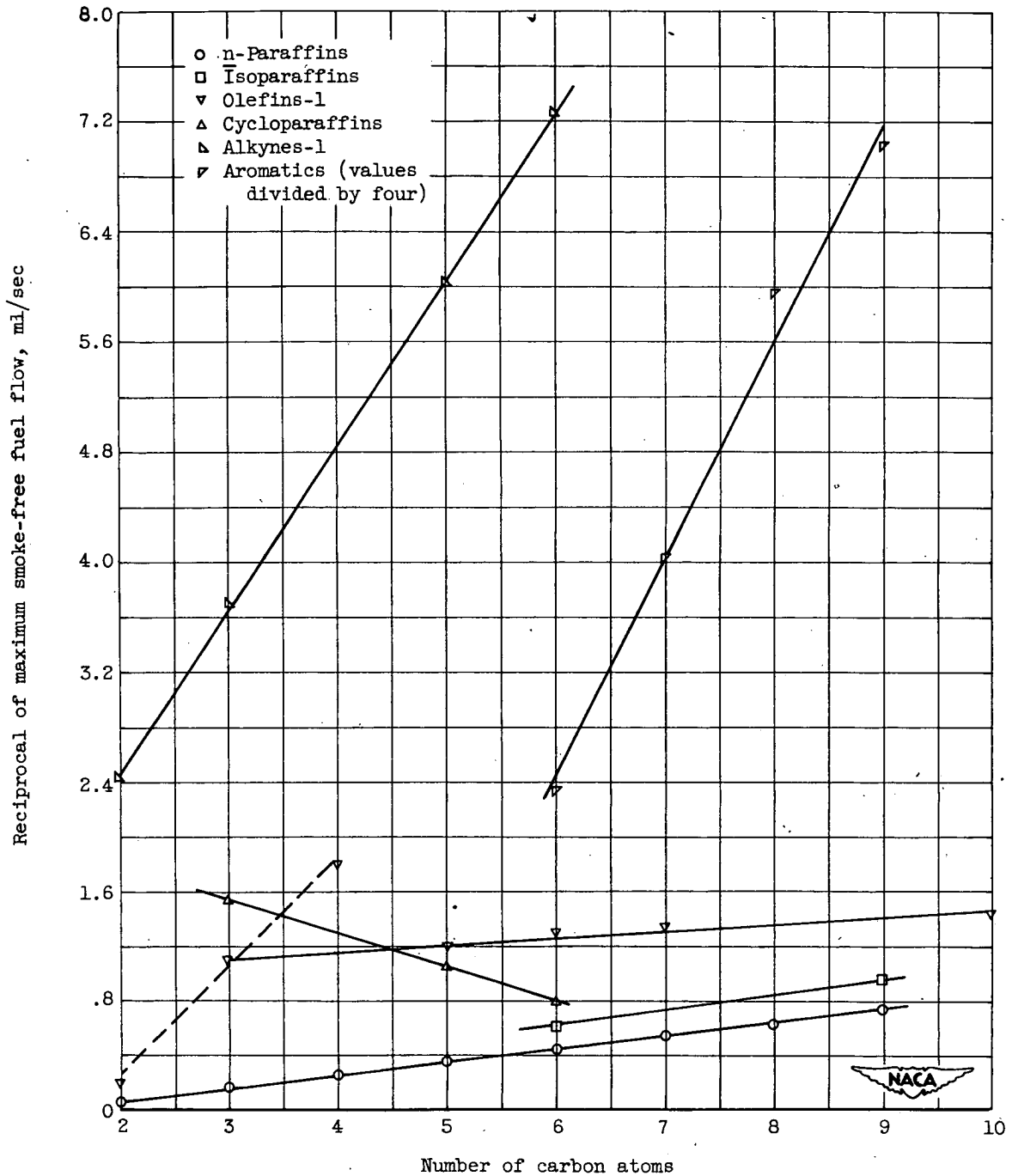


Figure 3. - Variation of reciprocal of maximum smoke-free fuel flow with number of carbon atoms.

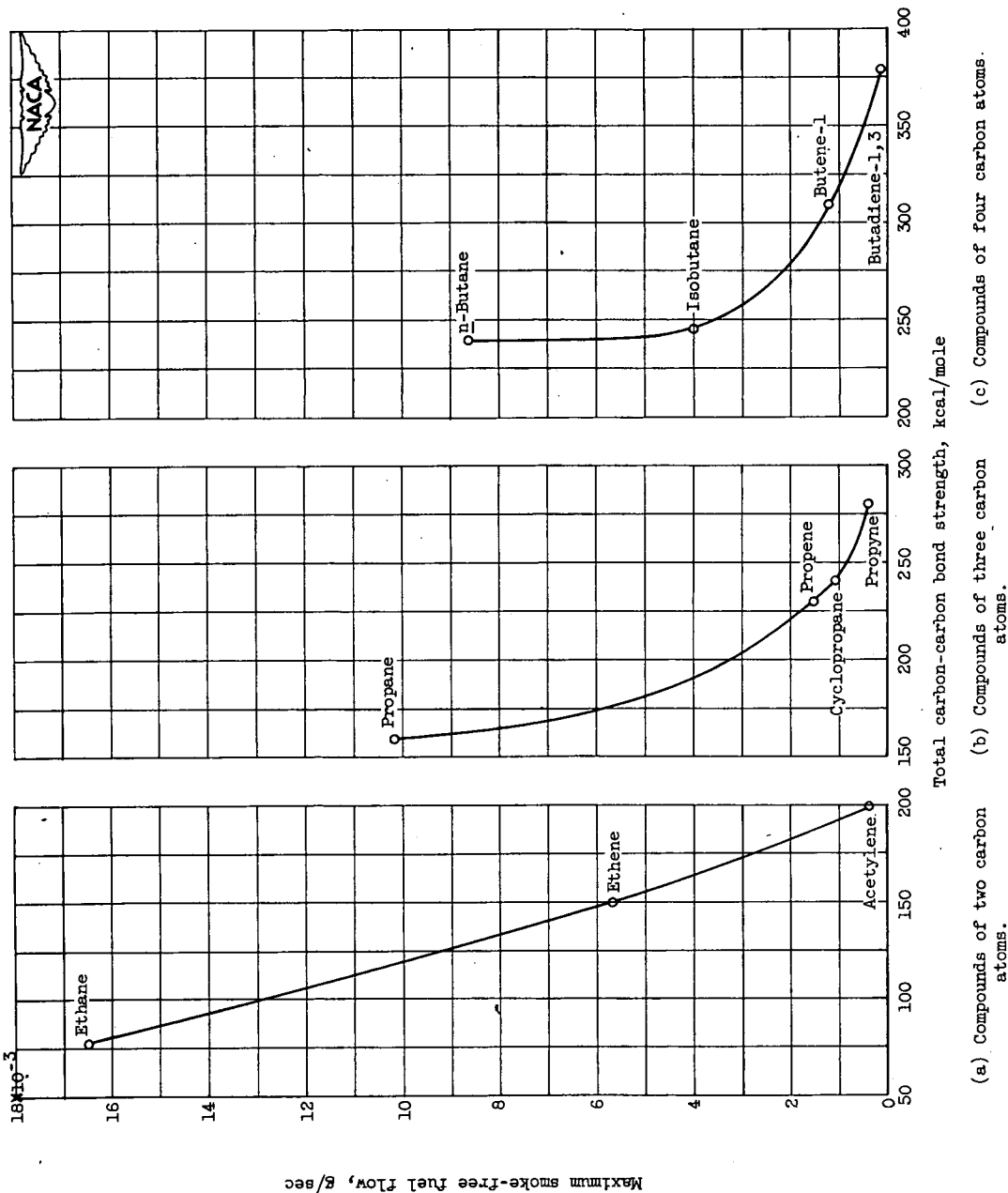


Figure 4. - Variation of maximum smoke-free fuel flow with carbon-carbon bond strength.

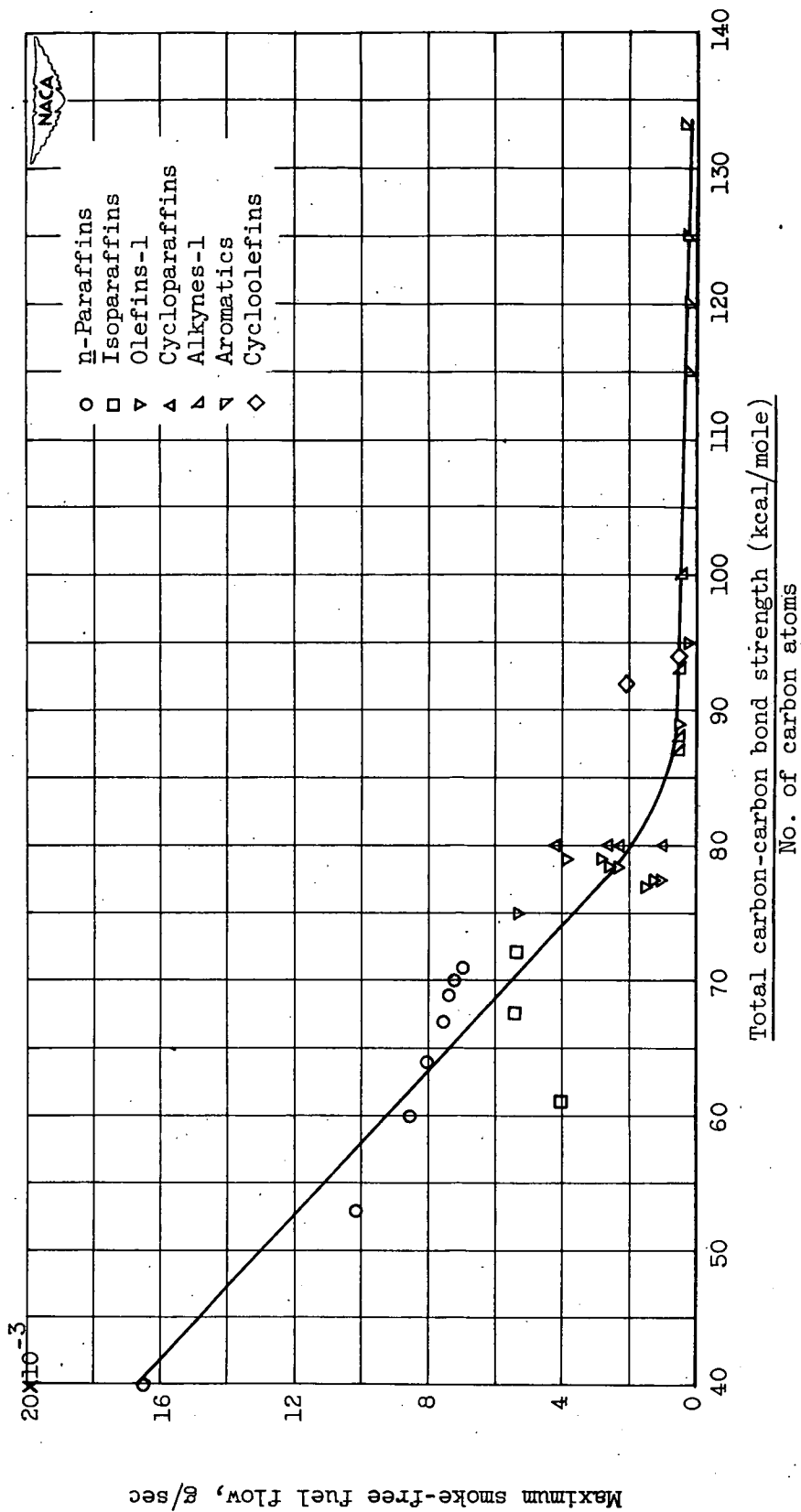


Figure 5. - Variation of maximum smoke-free fuel flow with total carbon-carbon bond strength per number of carbon atoms.